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AFRL/PRS
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9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

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62 separate items are enclosed

Ann C8

MEMORANDUM FOR PR (In-House Publication)

FROM: PROI (TI) (STINFO) 30 Jun 2000

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-TP-2000-144**
M. Fajardo, S. Tam, "High Resolution Infrared Absorption Spectroscopy in Doped Parahydrogen Solids: CO/pH_2 – a Molecular Thermometer"

3rd International Conference on Cryocrystals and Quantum Crystals (Statement A)
(Szklarska Poreba, Poland, 28 Jul – 04 Aug 00) (Submission Deadline: 28 Jul 00)

1. This request has been reviewed by the Foreign Disclosure Office for: a.) appropriateness of distribution statement, b.) military/national critical technology, c.) export controls or distribution restrictions, d.) appropriateness for release to a foreign nation, and e.) technical sensitivity and/or economic sensitivity.
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LESLIE S. PERKINS, Ph.D (Date)
Staff Scientist
Propulsion Directorate

3rd International Conference on Cryocrystals and Quantum Crystals, 28 Jul - 4 Aug 2000, Szklarska Poreba, Poland

High Resolution Infrared Absorption Spectroscopy in Doped Parahydrogen Solids: CO/pH_2 -- a Molecular Thermometer

Mario E. Fajardo, and Simon Tam
USAF Research Laboratory, AFRL/PRSP, Bldg. 8451, Edwards AFB, CA 93524-7680
mario_fajardo@plc.af.mil

* HEDM Cryosolid Propellants
* Trapping of Metal Atoms in Cryogenic Solid Hydrogen
* Rapid Vapor Deposition of Transparent Parahydrogen (pH_2) Solids
* High Resolution IR Absorption Spectroscopy in Doped pH_2 Solids
* CO/pH_2 "Thermometer" Depositions
* Summary

HEDM Cryosolid Propellants Payoffs

Increased Specific Impulse

$$I_{sp} \propto \sqrt{\Delta H_{sp}}$$

$$LOX/LH_2 : I_{sp} = 390 \text{ s}$$
$$5\% \text{ B/s}H_2 + LOX : I_{sp} = 500 \text{ s } (+30\%)^*$$

* calculated for $P_{chamber} = 1000$ PSIA, $P_{exhaust} = 14.7$ PSIA

Greater Propellant Density

$$\text{liquid } H_2 \text{ @ } 20 \text{ K} : \rho = 0.070 \text{ g/cm}^3$$
$$\text{solid } H_2 \text{ @ } 2 \text{ K} : \rho = 0.087 \text{ g/cm}^3 \ (+25\%)$$
$$50/50 \text{ liquid He/solid } H_2 : \rho = 0.105 \text{ g/cm}^3 \ (+50\%)$$

Dopant recombination/reaction in solid pH_2

* ideally:

$$X + pH_2 \xrightarrow{T=2K} X/pH_2$$ isolated atoms

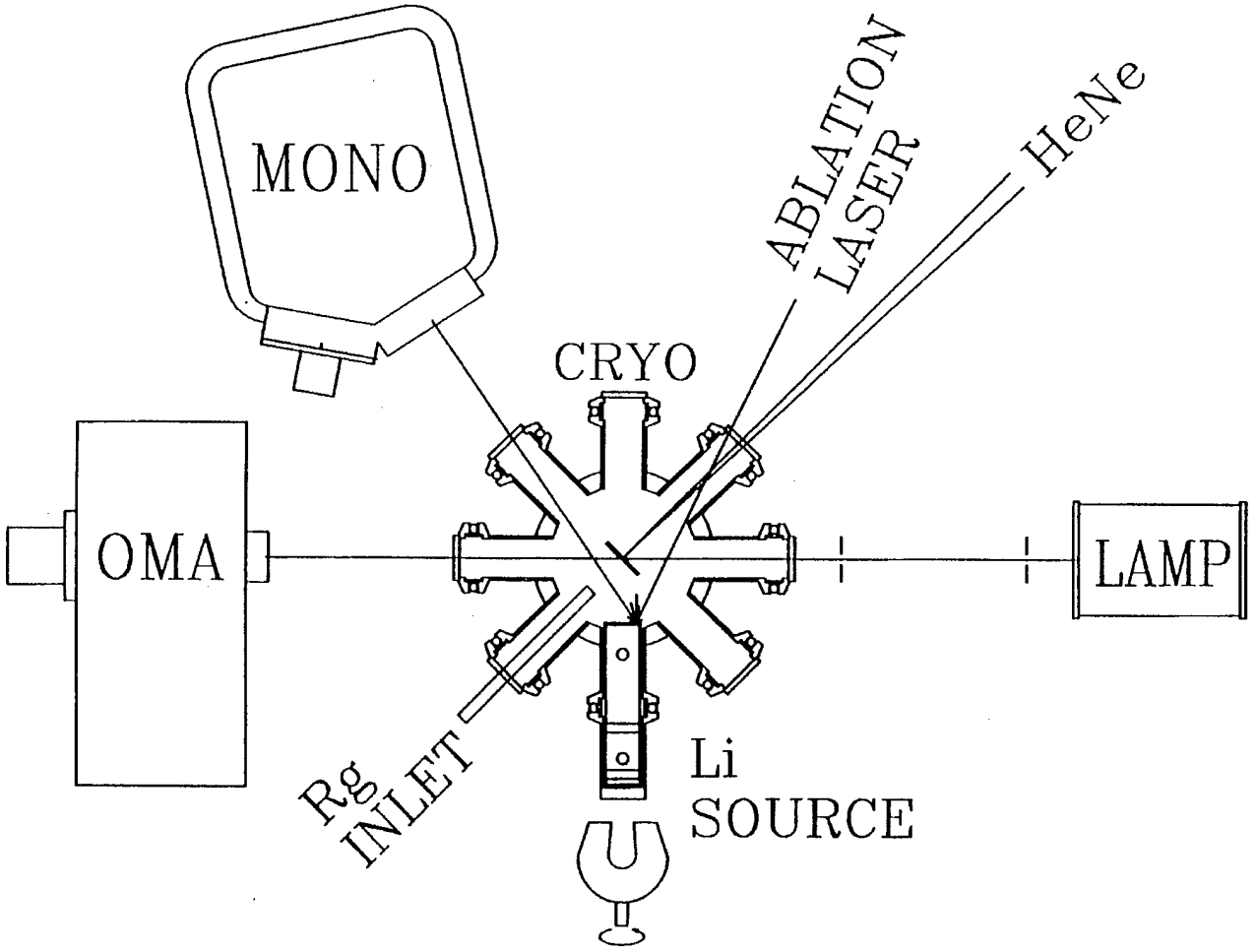
* in practice:

$$X + X + M \rightarrow X_2 + M$$ recombination
$$\rightarrow X_n$$

$$X + H_2 + M \rightarrow HX + H + M$$ reaction
$$\rightarrow H_nX + M$$

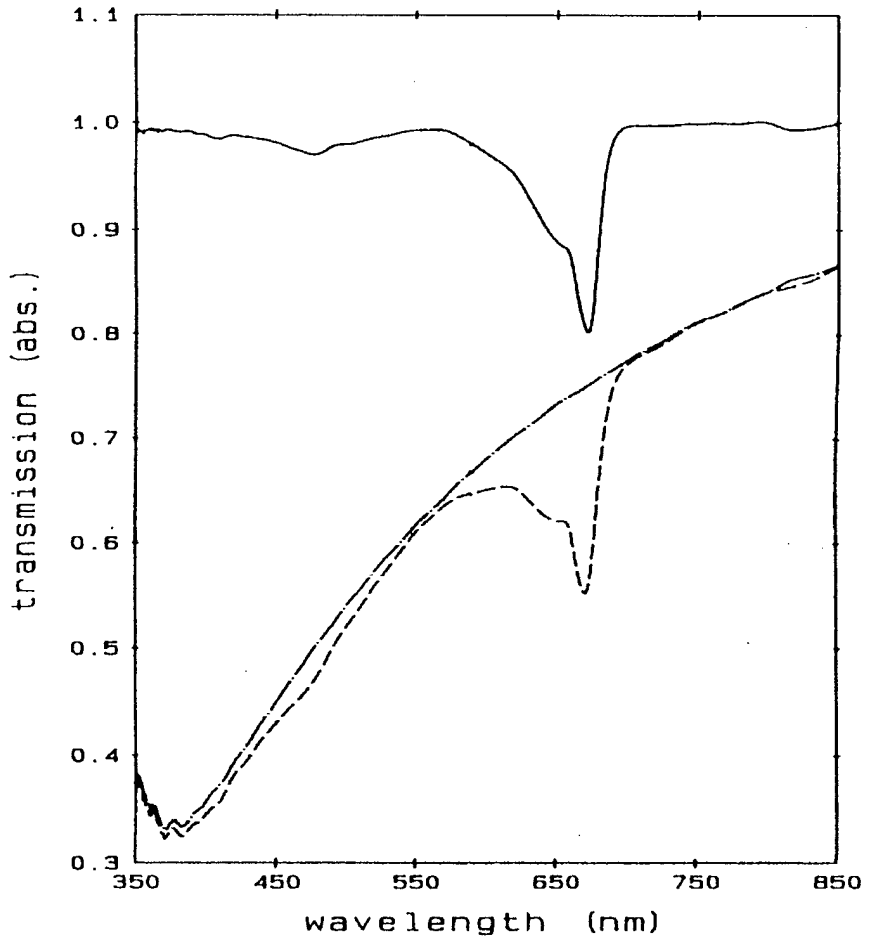
$$X_n + H_2 + M \rightarrow HX_n + H + M$$ both
$$\rightarrow H_mX_n + M$$

Experimental Diagram (c1993)



M.E. Fajardo, J. Chem. Phys. **98**, 110 (1993).

Transmission Spectrum of Li/nH_2, d ≈ 10 μ



—— difference + 1.0

—·— pure pH_2

------ Li/pH_2

M.E. Fajardo, J. Chem. Phys. **98**, 110 (1993).

Optical Scattering in Solid Hydrogen

Crystal Growing and Quality (p. 81)

"There is a considerable art to growing hydrogen crystals of high quality. Good crystals are always grown slowly from the melt; a rapid freeze from the gas produces snow."

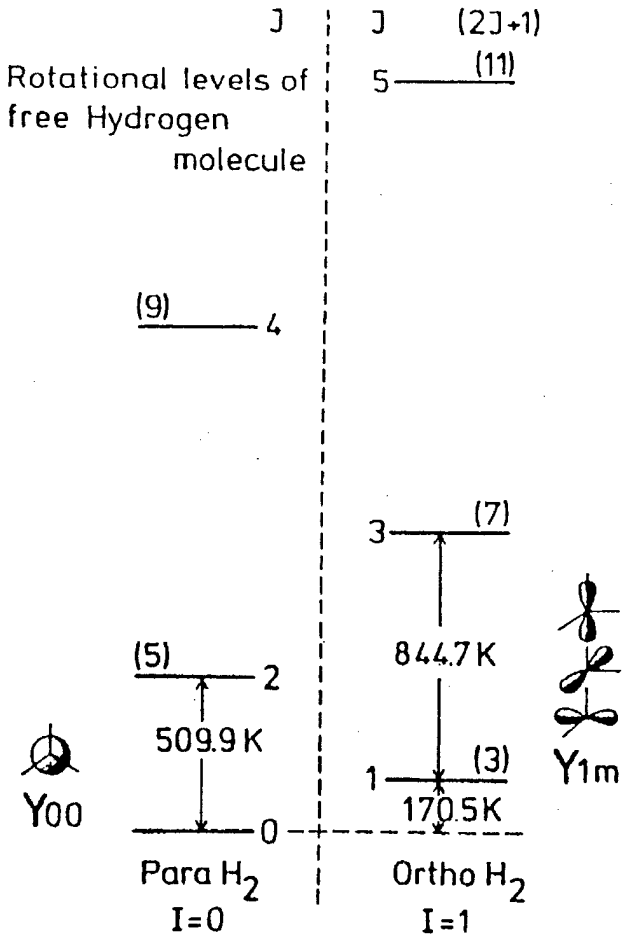
Crystallite Light Scattering (p. 83)

"The reason that a good hydrogen crystal is so hard to see is its low refractive index...an estimated 1.16!

Yet a 1 mm-thick layer of hydrogen crystallites can be a completely opaque brown-black."

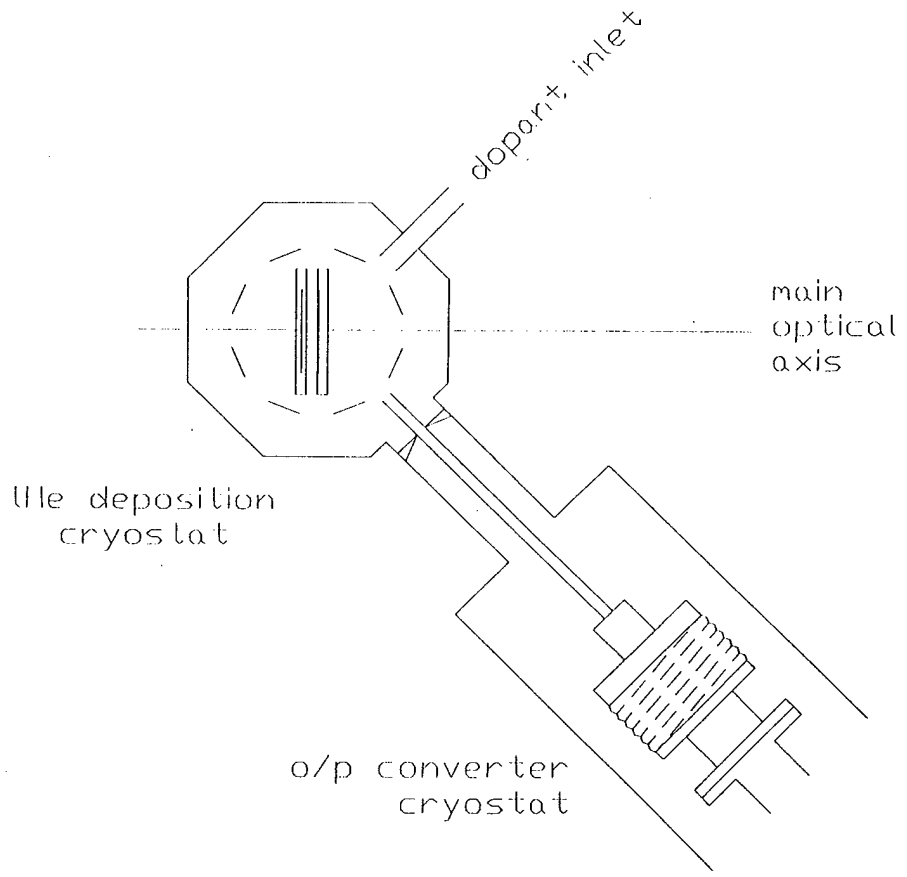
[P.C. Souers, Hydrogen Properties for Fusion Energy (UC Press, Berkeley, 1986)]

ortho- and para-hydrogen



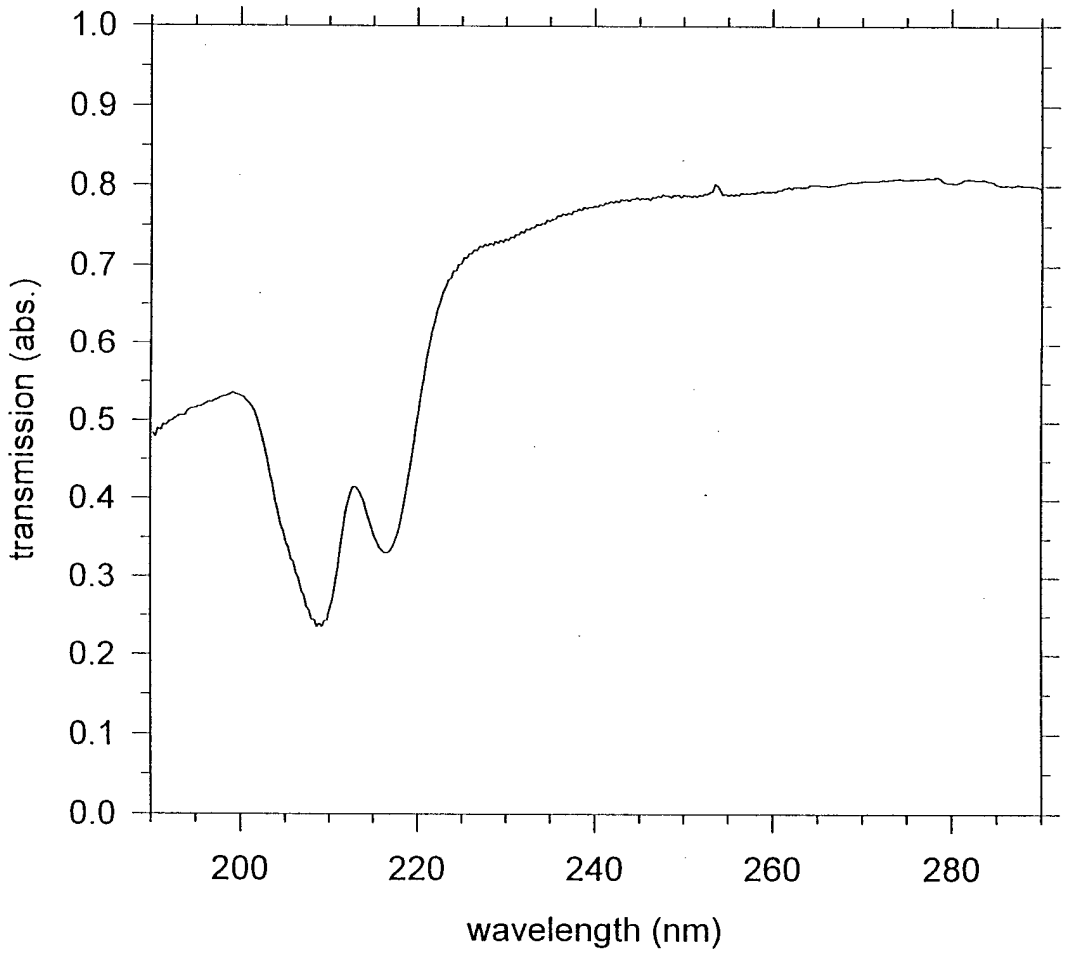
[I.F. Silvera, Rev. Mod. Phys. **52**, 393 (1980)]

Experimental Diagram (c1997)



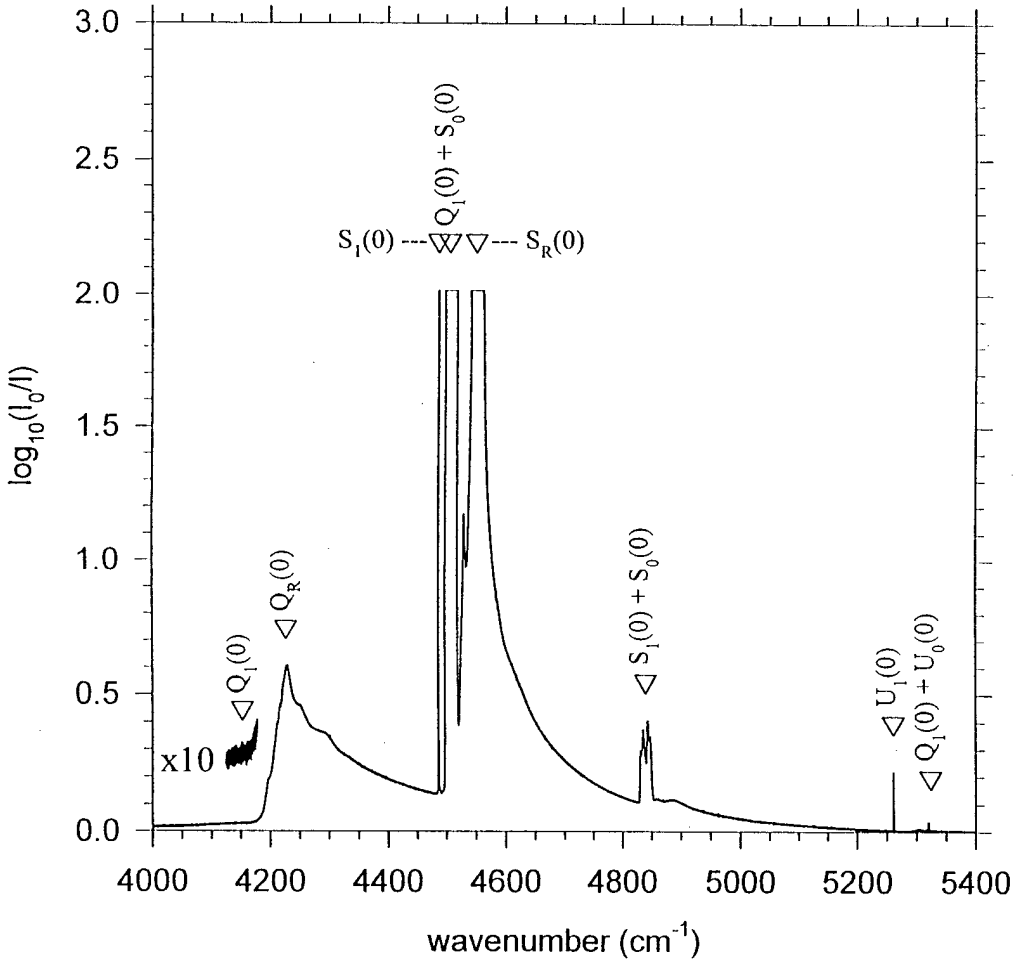
M.E. Fajardo and S. Tam, J. Chem. Phys. **108**, 4237 (1998).
S. Tam and M.E. Fajardo, Rev. Sci. Instrum. **70**, 1926 (1999).

Transmission Spectrum of B/pH_2 d≈1mm



M.E. Fajardo and S. Tam, J. Chem. Phys. **108**, 4237 (1998).
S. Tam, M. Macler, M.E. DeRose, and M.E. Fajardo, J. Chem. Phys., submitted (2000).

IR Absorption of 6 mm Thick pH_2 Solid



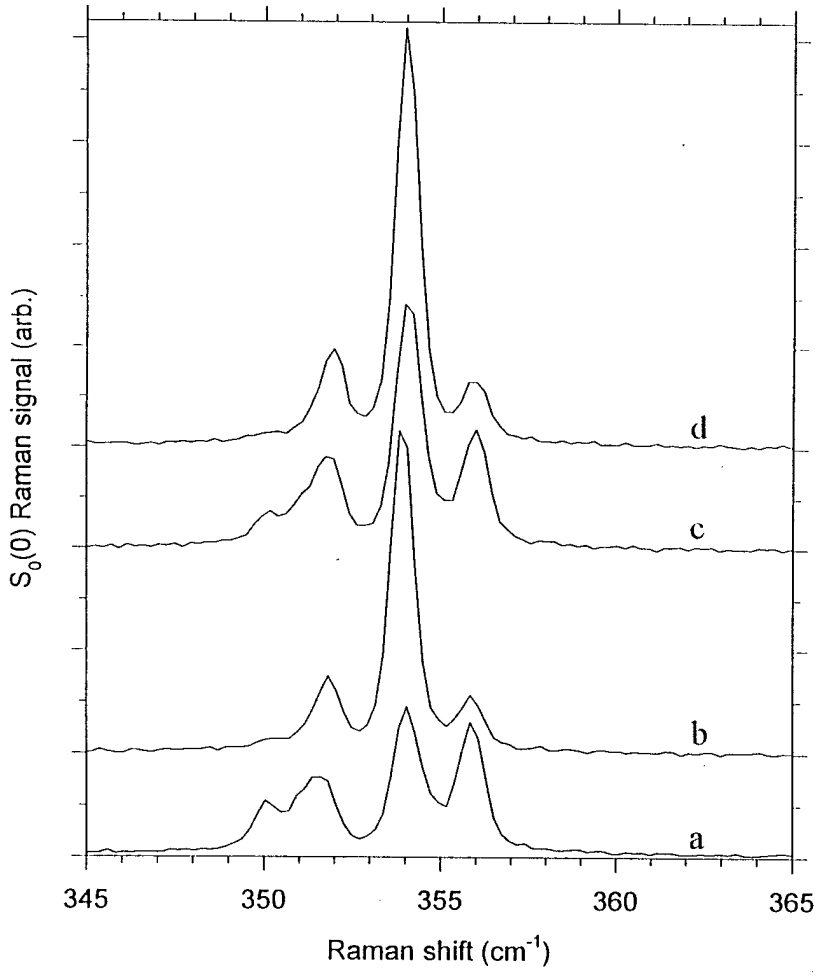
Non-observation of the $Q_1(0)$ transition demonstrates the absence of oH_2 impurities, and that the microscopic structure is not amorphous or porous.

Observation of $S_1(0)$ transition demonstrates the absence of inversion symmetry for <u>some</u> H_2 molecular environments.

[van Kranendonk and Gush, Phys. Lett. **1**, 22 (1962)]

M.E. Fajardo and S. Tam, J. Chem. Phys. **108**, 4237 (1998).

Raman Spectra of pH_2 Solids



Mixed hcp/fcc as-deposited structure, anneals to hcp.
[G.W. Collins, et al., Phys. Rev. B **53**, 102 (1996)]

(d) sample in (c) warmed to 4.5 K.
(c) 4.5 mm sample as deposited at 3.3 K (Φ = 290 mmol/hr).

(b) sample in (a) warmed to 4.5 K.
(a) 6 mm sample as deposited at 3.1 K (Φ = 200 mmol/hr).

M.E. Fajardo and S. Tam, J. Chem. Phys. **108**, 4237 (1998).

High Res. IR Spectroscopy in Solid pH_2

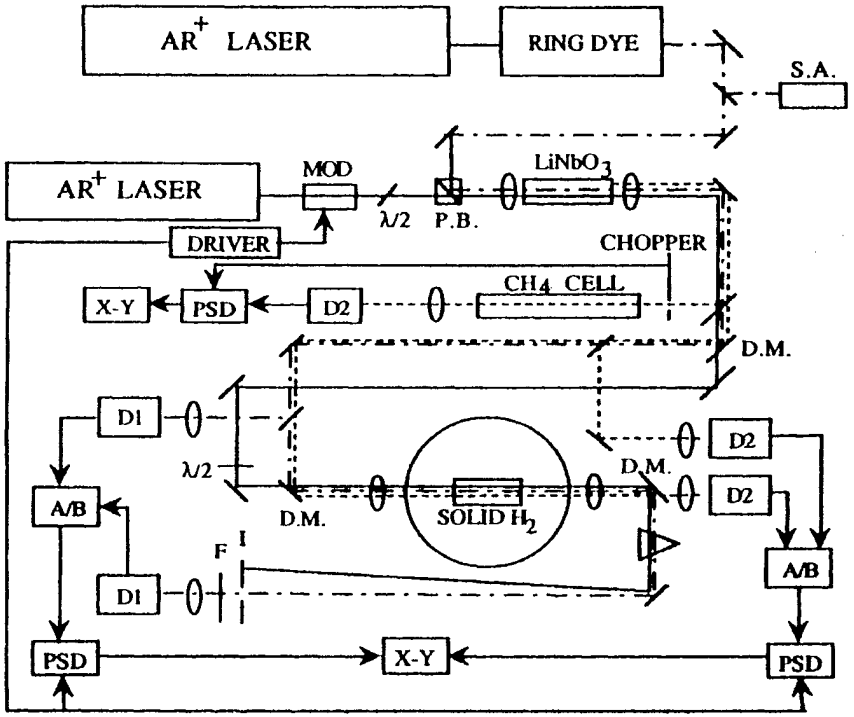
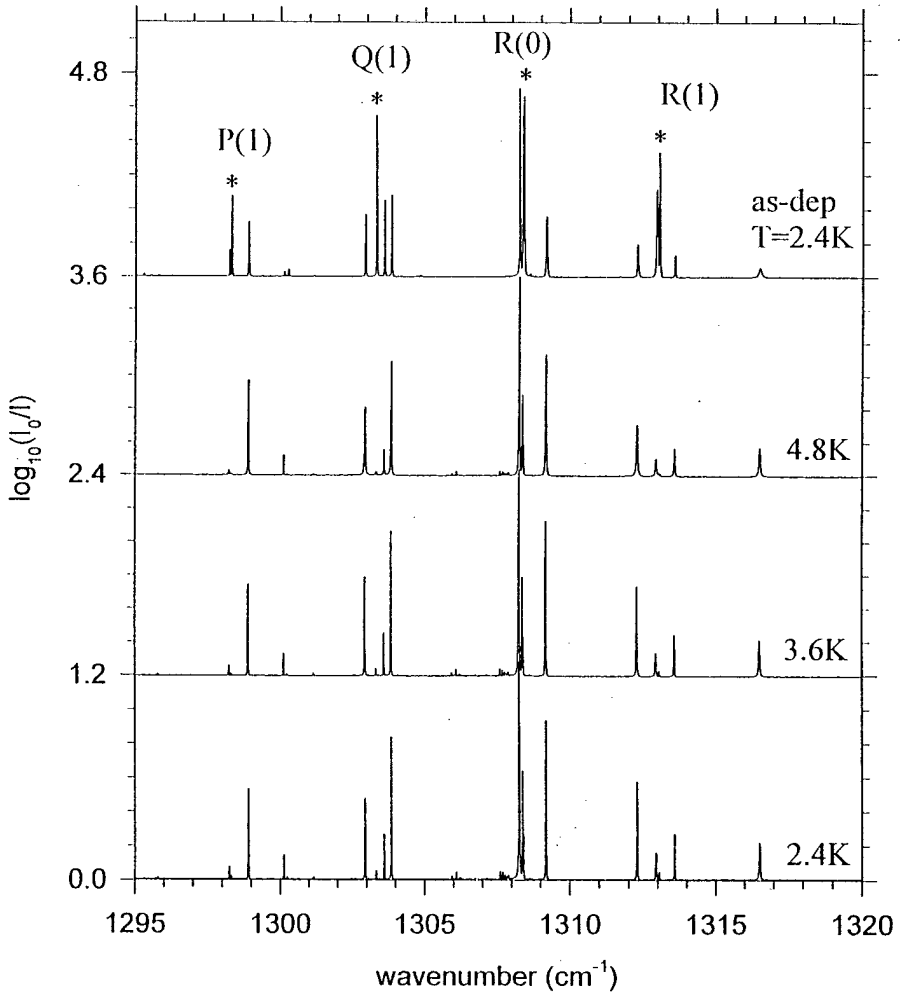


FIG. 1. Apparatus for the simultaneous spectroscopy of the infrared and Raman transitions. The nonlinearity of $LiNbO_3$ is used for the former and that of solid H_2 is used for the latter. D.M., dichroic mirror; S. A., spectrum analyzer; P. B., polarizer beamsplitter.

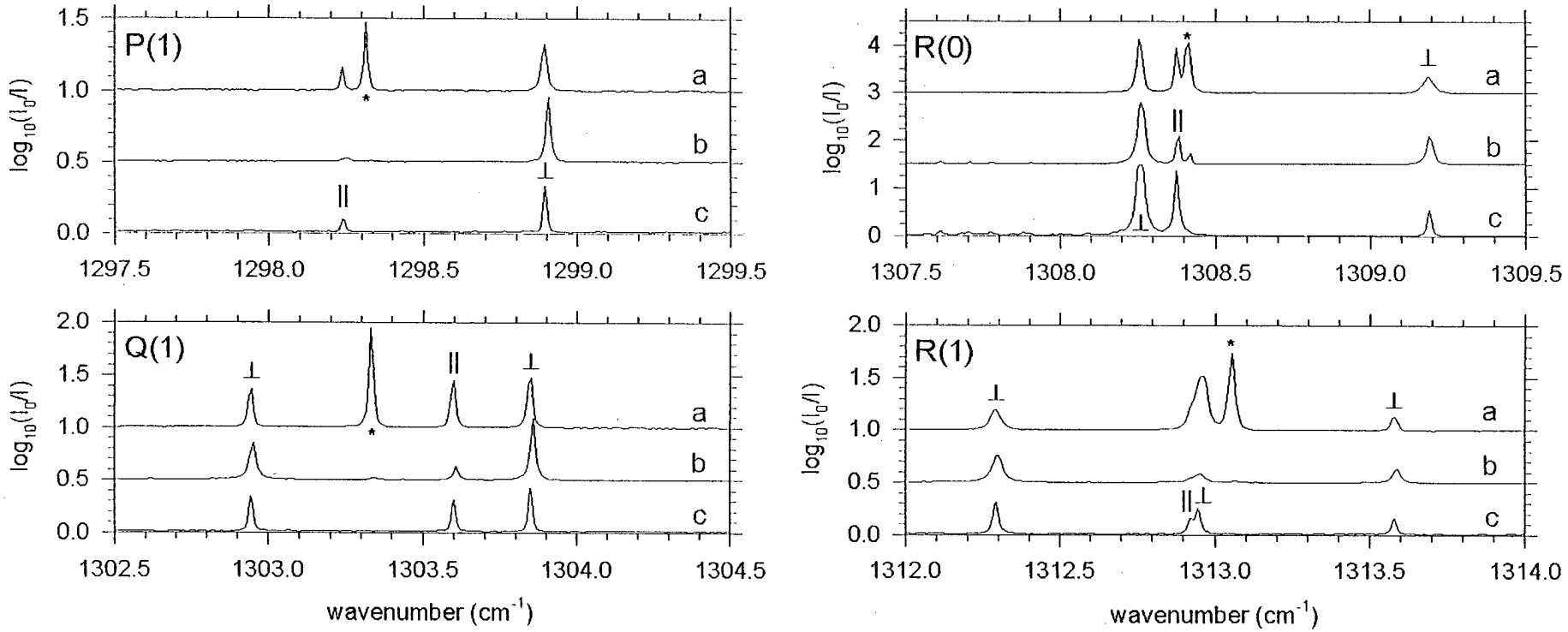
[T. Momose, K.E. Kerr, D.P. Weliky, C.M. Gabrys, R.M. Dickson and T. Oka, J. Chem. Phys. **100**, 7840 (1994)]

ν_4 CH_4/pH_2 IR Absorptions (res = 0.01 cm^{-1})



S. Tam, M.E. Fajardo, H. Katsuki, H. Hoshina, T. Wakabayashi, and T. Momose, J. Chem. Phys. **111**, 4191 (1999).

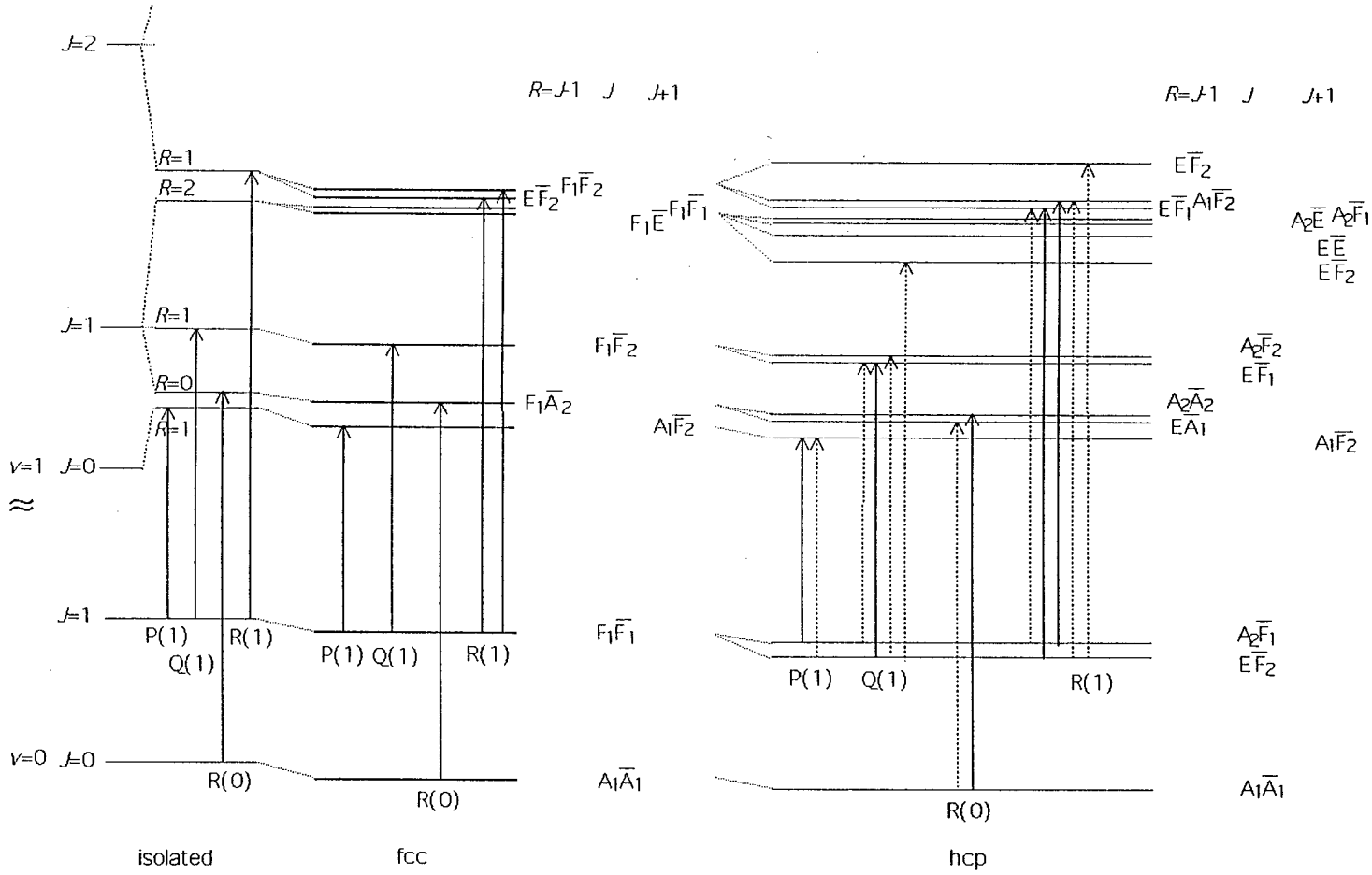
ν_4 CH_4/pH_2 IR Absorptions



(a) Rapid Vapor Deposited sample: as-deposited at 2.4 K
(b) Rapid Vapor Deposited sample: annealed to 4.8 K
(c) Enclosed Cell Condensed sample: cooled to 4.8 K

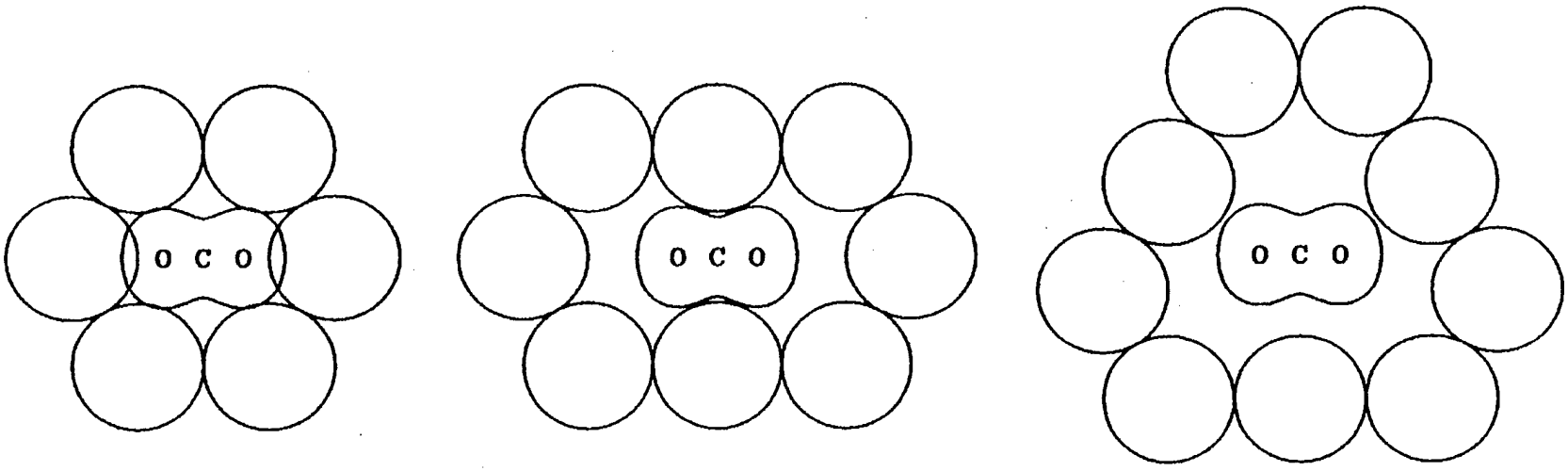
S. Tam, M.E. Fajardo, H. Katsuki, H. Hoshina, T. Wakabayashi, and T. Momose, J. Chem. Phys. **111**, 4191 (1999).

ν_4 CH_4/pH_2 Energy Levels



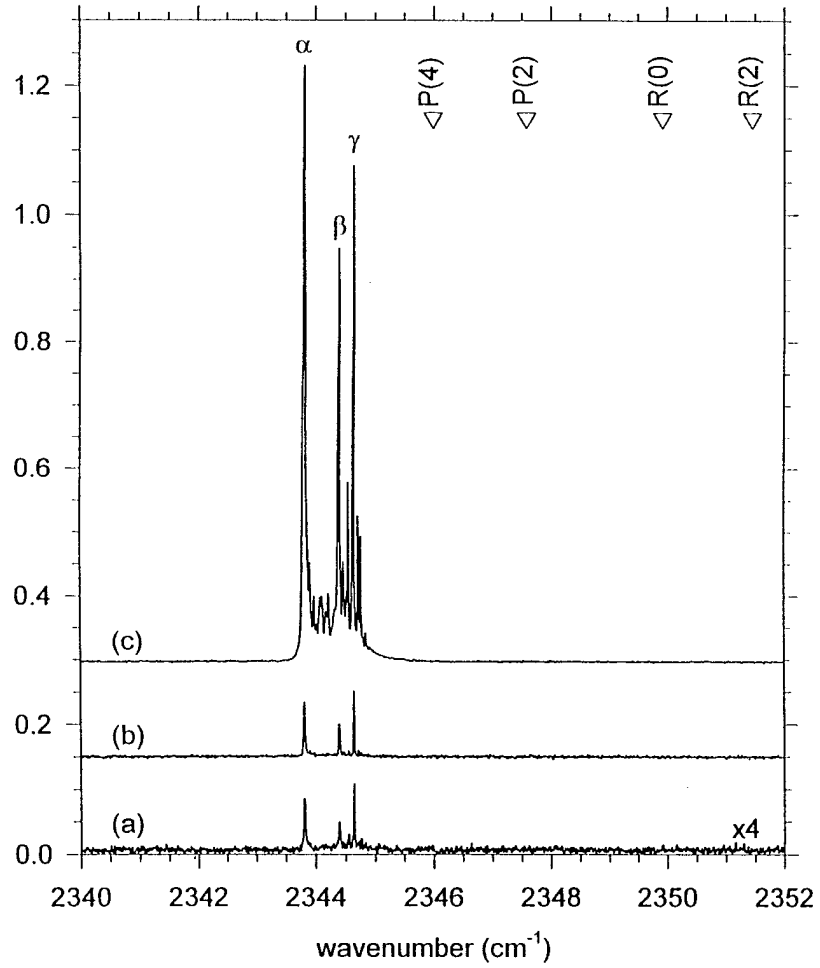
S. Tam, M.E. Fajardo, H. Katsuki, H. Hoshina, T. Wakabayashi, and T. Momose, J. Chem. Phys. **111**, 4191 (1999).

CO_2/pH_2 Trapping Sites



S. Tam and M.E. Fajardo, Fiz. Nizk. Temp. [Low Temp. Phys.] accepted (2000).

CO_2/pH_2 IR Absorptions (res = 0.008 cm^{-1})



as-deposited at T = 2.4 K

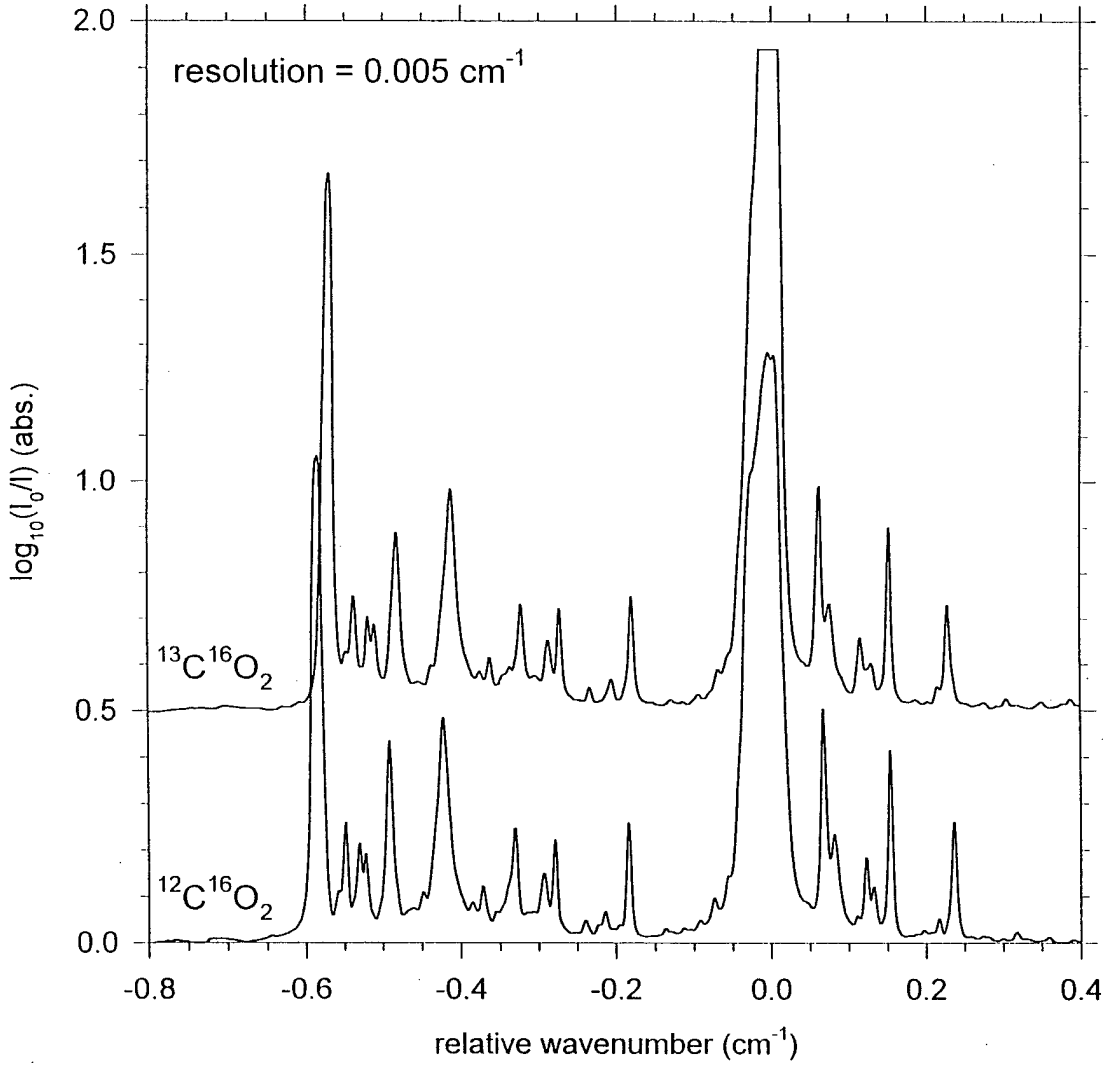
(c) 1.2 ppm CO_2/pH_2

(b) 0.04 ppm CO_2/pH_2

(a) 0.01 ppm CO_2/pH_2

S. Tam and M.E. Fajardo, Fiz. Nizk. Temp. [Low Temp. Phys.] accepted (2000).

$^{13}C^{16}O_2/pH_2$ vs. $^{12}C^{16}O_2/pH_2$

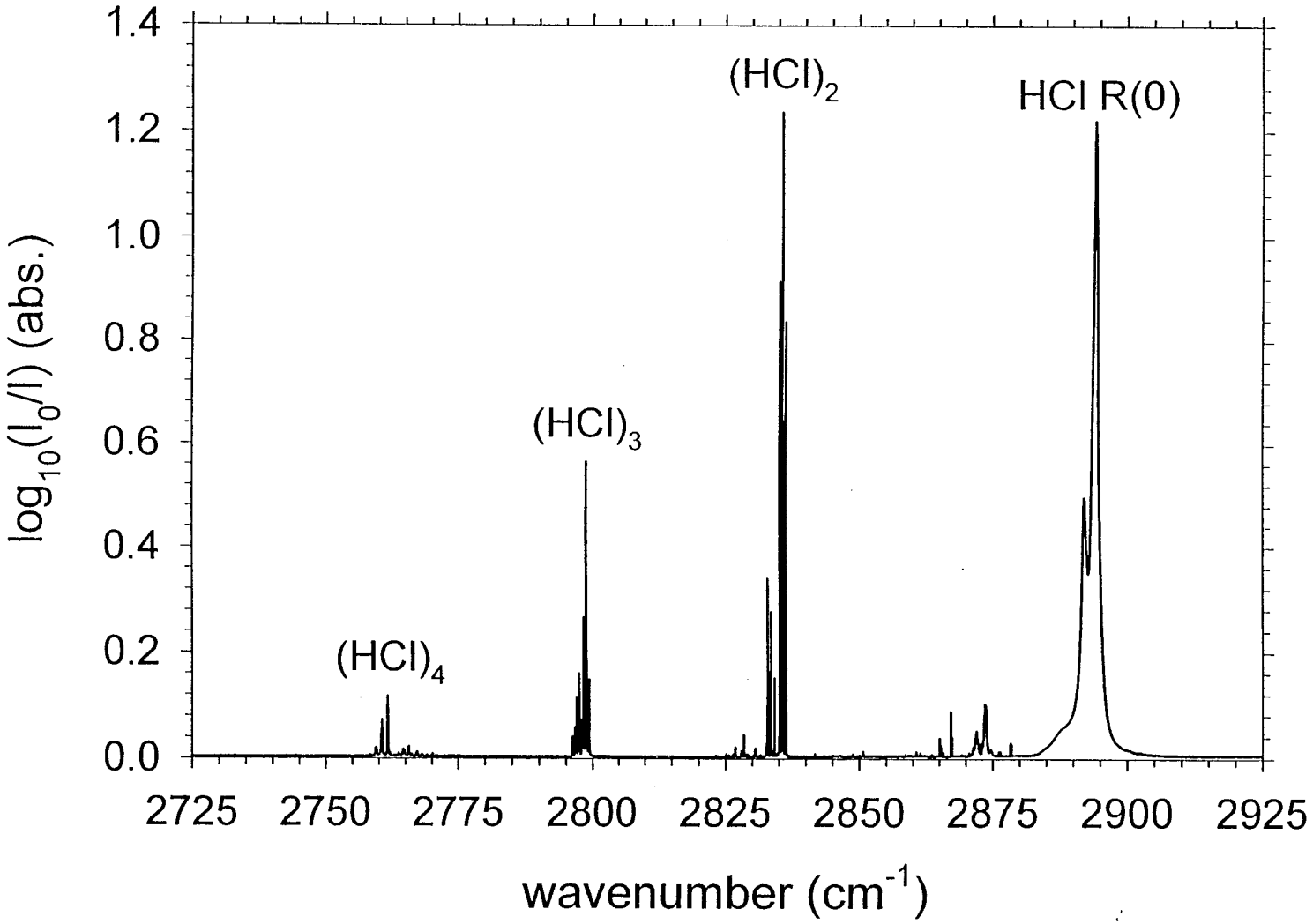


annealed, T = 2.4 K

d = 1.0 mm

2 ppm $^{13}C^{16}O_2$ and
2 ppm $^{12}C^{16}O_2$

88 PPM HCl/pH_2



Gas Phase $(HCl)_2$

High resolution, jet-cooled infrared spectroscopy of $(HCl)_2$: Analysis of ν_1 and ν_2 HCl stretching fundamentals, interconversion tunneling, and mode-specific predissociation lifetimes

Michael D. Schuder,[a] Christopher M. Lovejoy,[b] Robert Lascola,[c] and David J. Nesbitt[d]
Joint Institute for Laboratory Astrophysics, National Institute of Standards and Technology and University of Colorado, and the Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309

(Received 5 April 1993; accepted 7 June 1993)

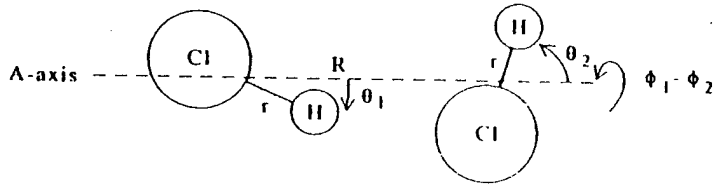
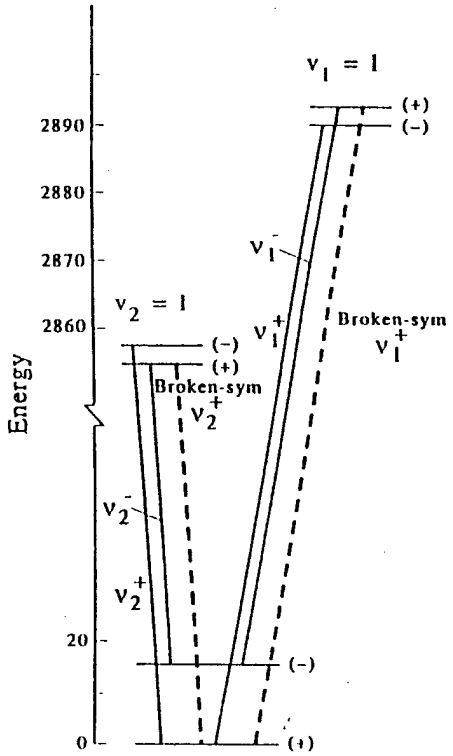
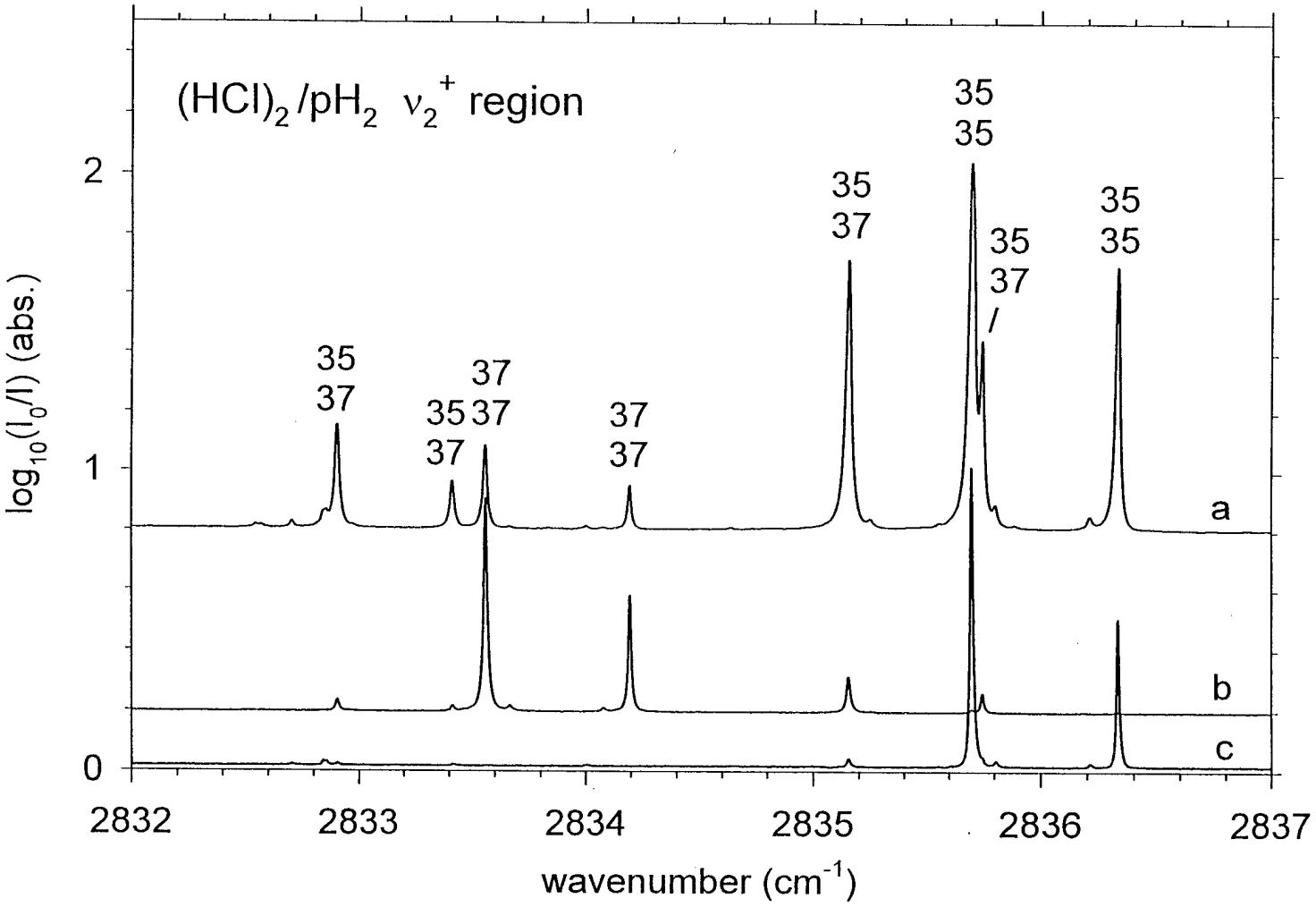


FIG. 1. Vibrationally averaged structure and internal coordinates for HCl dimer. The intermolecular axis R connects the HCl centers of mass. The internal angles, θ_1 and θ_2, are measured from the intermolecular axis to the HCl bonds r. The torsion angle, $\phi=\phi_1-\phi_2$, is shown at 180° (planar). The minimum energy configuration shown is for $\theta_1=16°$, $\theta_2=87°$ with $\phi_1-\phi_2=180°$. The HCl subunit on the left is referred to as the bonded HCl with an associated vibration labeled ν_2. The proton on the other HCl is not involved with the hydrogen bond, and this subunit is referred to as the free HCl, with a vibration labeled ν_1.

J. Chem. Phys. v99, p4346 (1993).

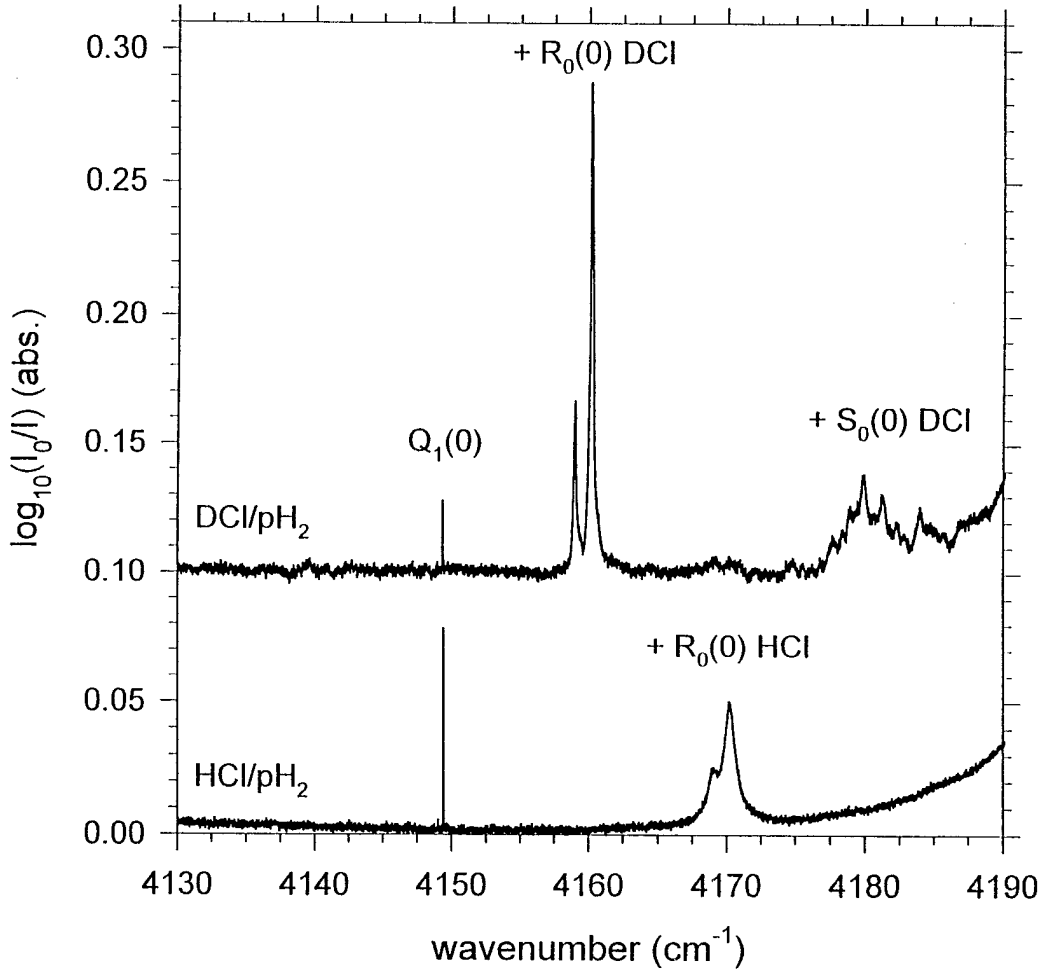


$(HCl)_2/pH_2$ isotopomers



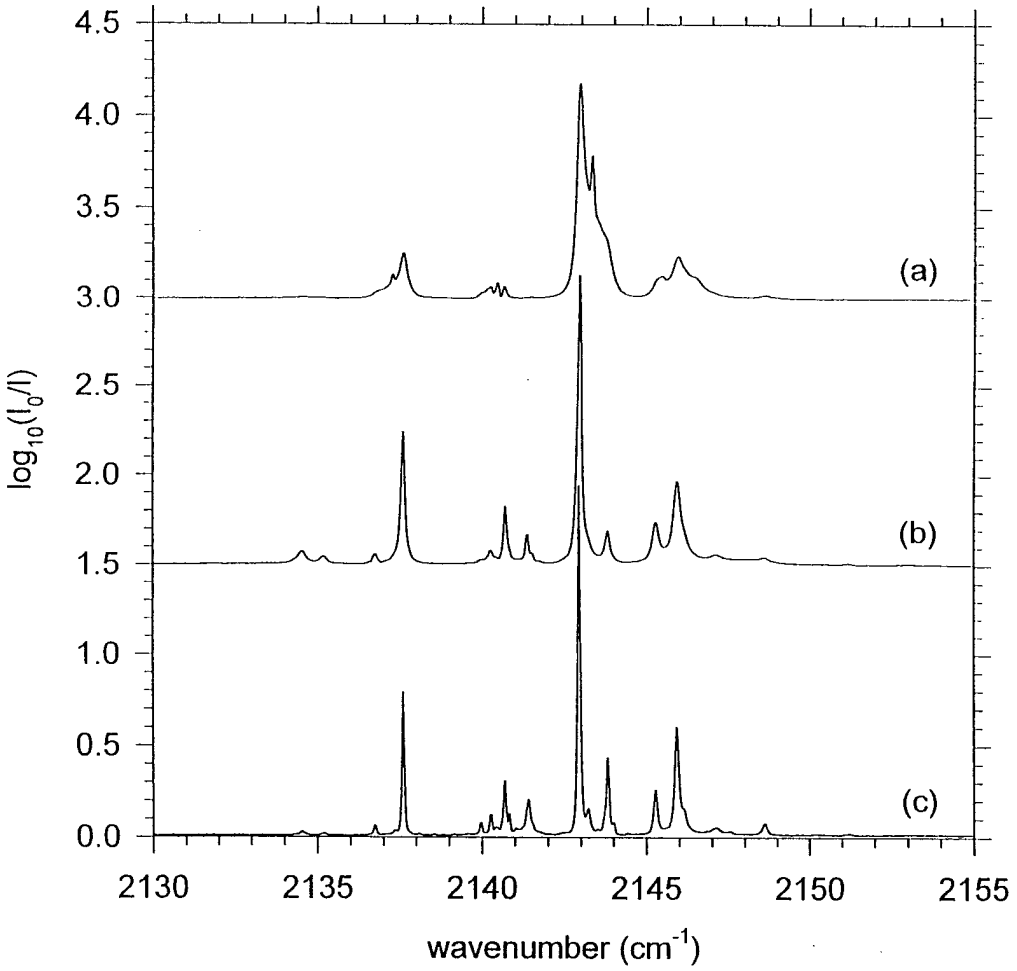
analysis in collaboration with D.T. Anderson, U. Wyoming.

Co-operative IR absorptions



analysis in collaboration with R.J. Hinde, U. Tennessee, Knoxville.

80 PPM CO/pH_2 (res = 0.1 cm^{-1})



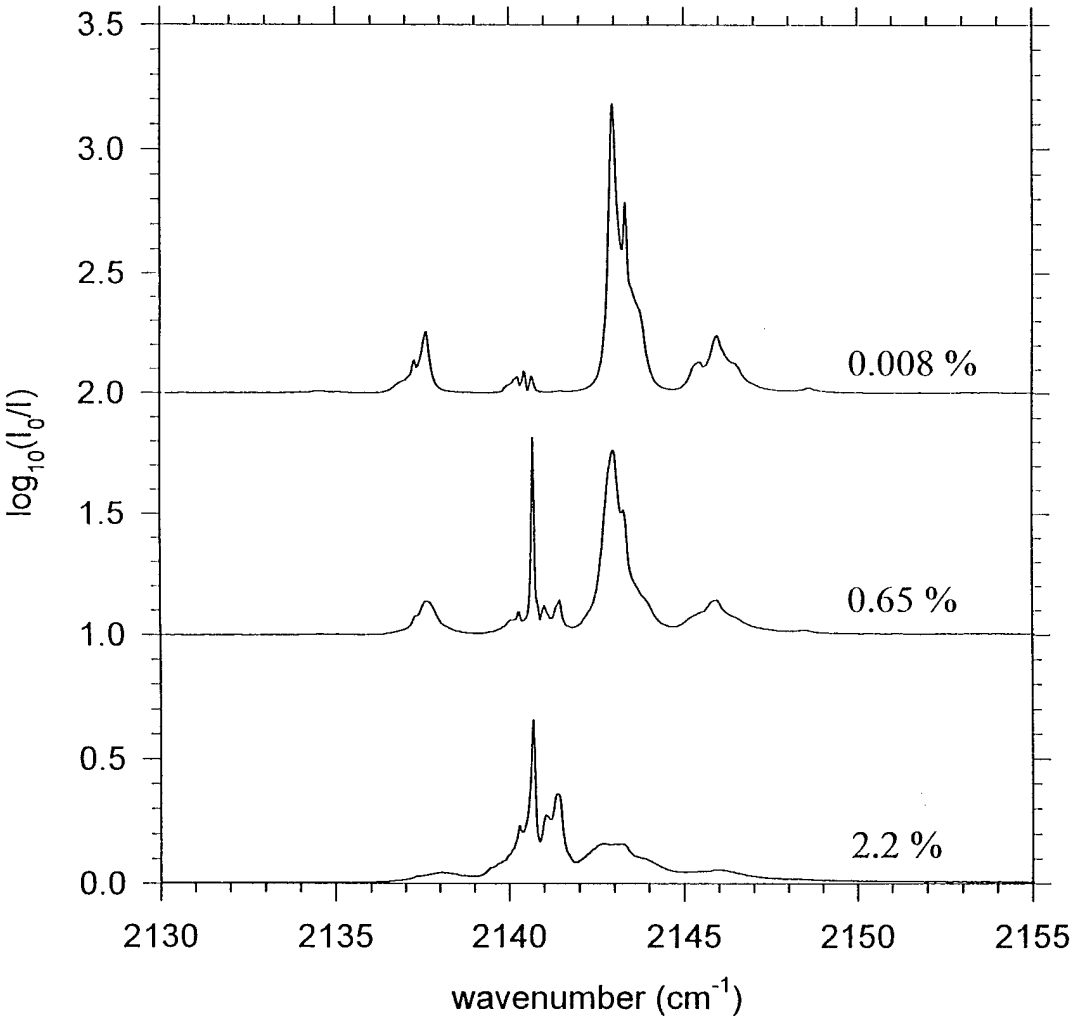
(a) as deposited at T = 2.4 K

(b) warmed to T = 4.8 K

(c) re-cooled to T = 2.4 K

analysis in collaboration with T. Momose, Kyoto U.

$(CO)_n/pH_2$ IR Absorptions



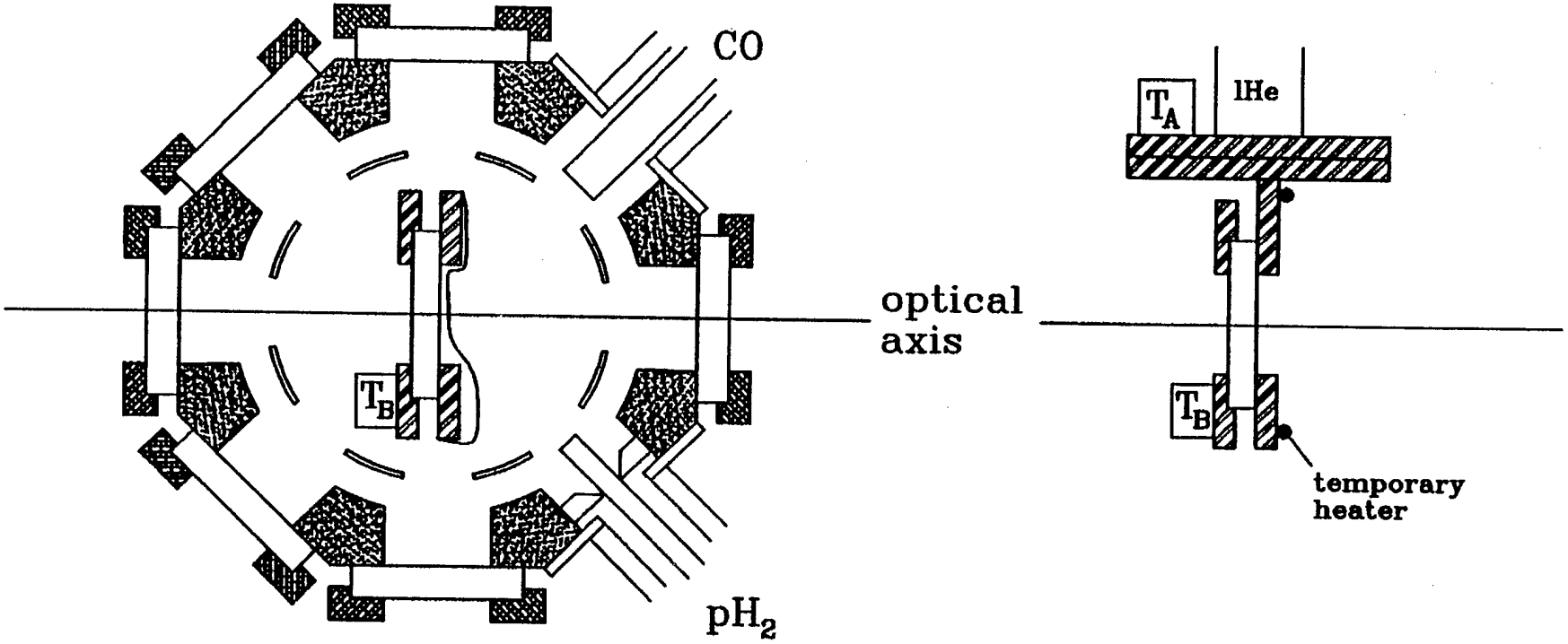
≈ 6 μmol CO in each sample

d = 1.7 mm

d = 20 μm

d = 4.7 μm

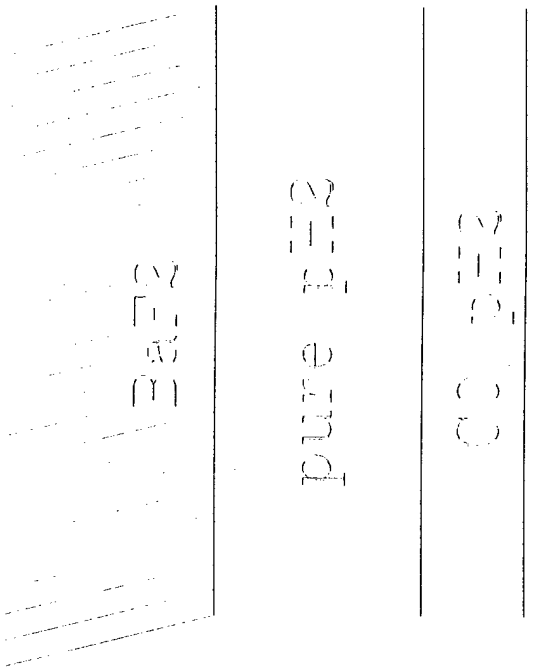
Experimental Diagram



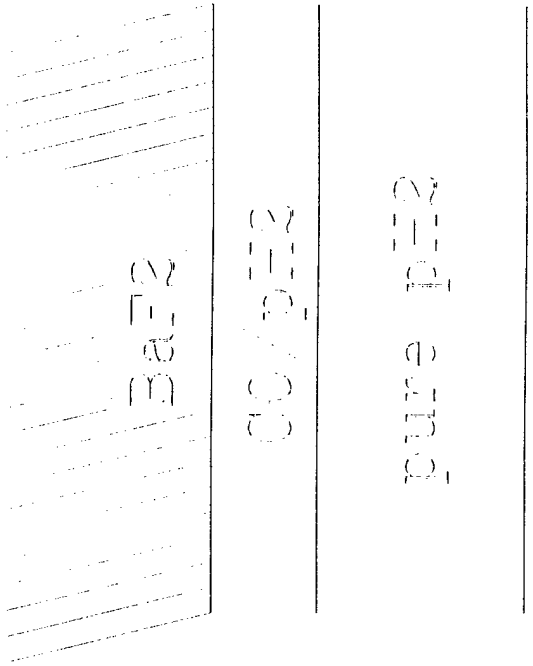
Top View

Side View

Experimental Protocol

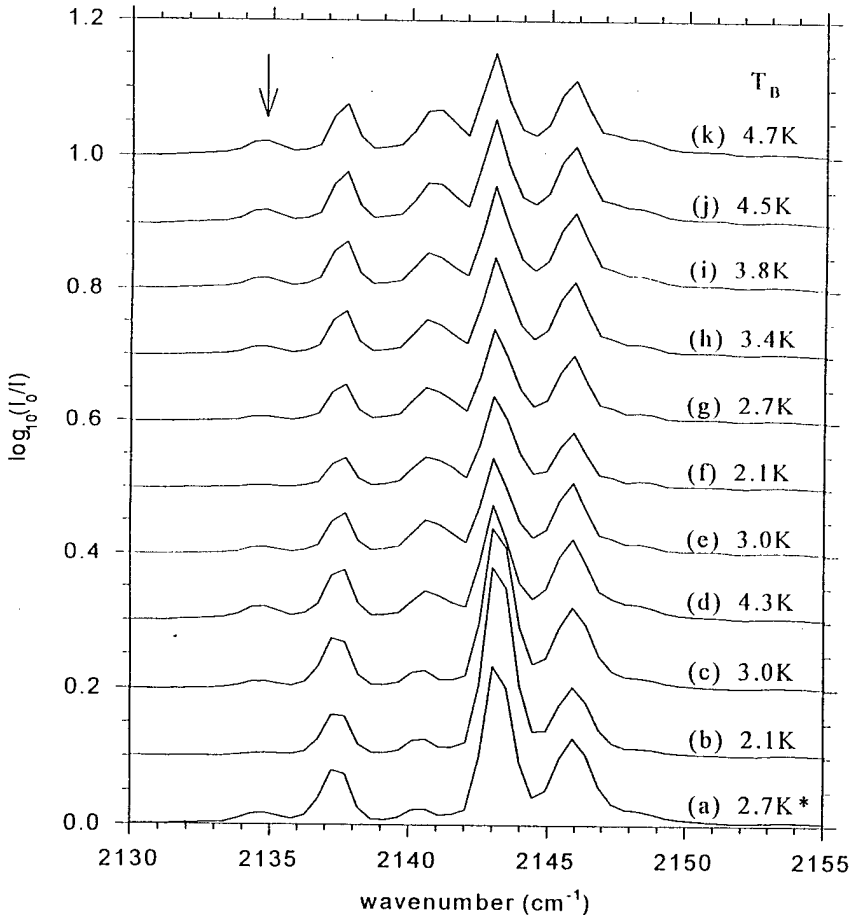


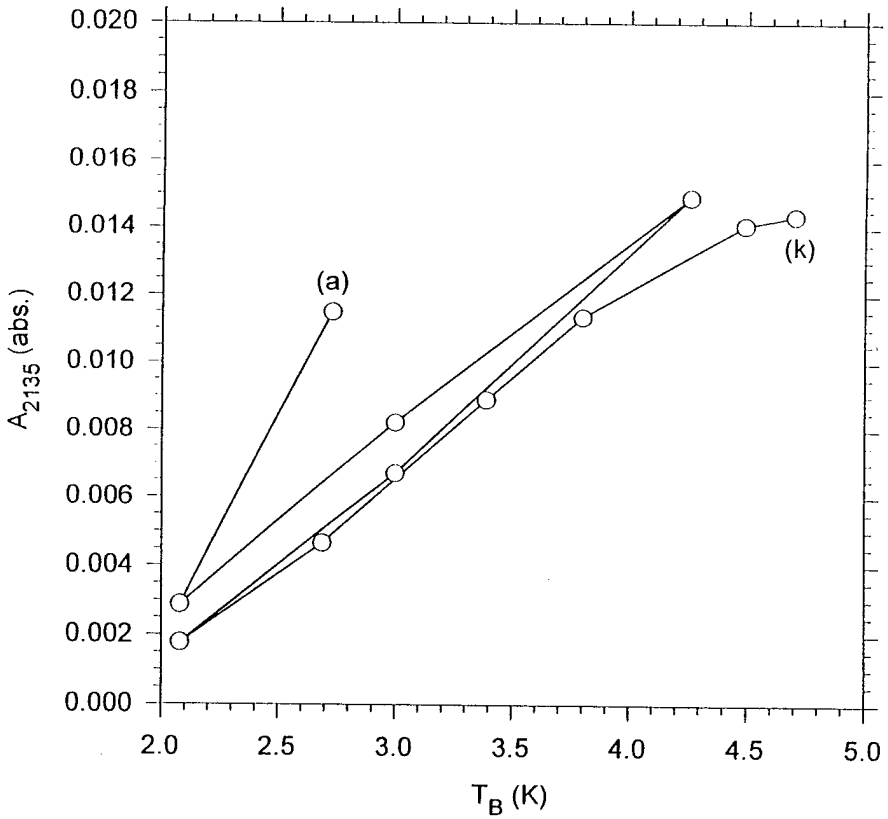
Thermometer experiments



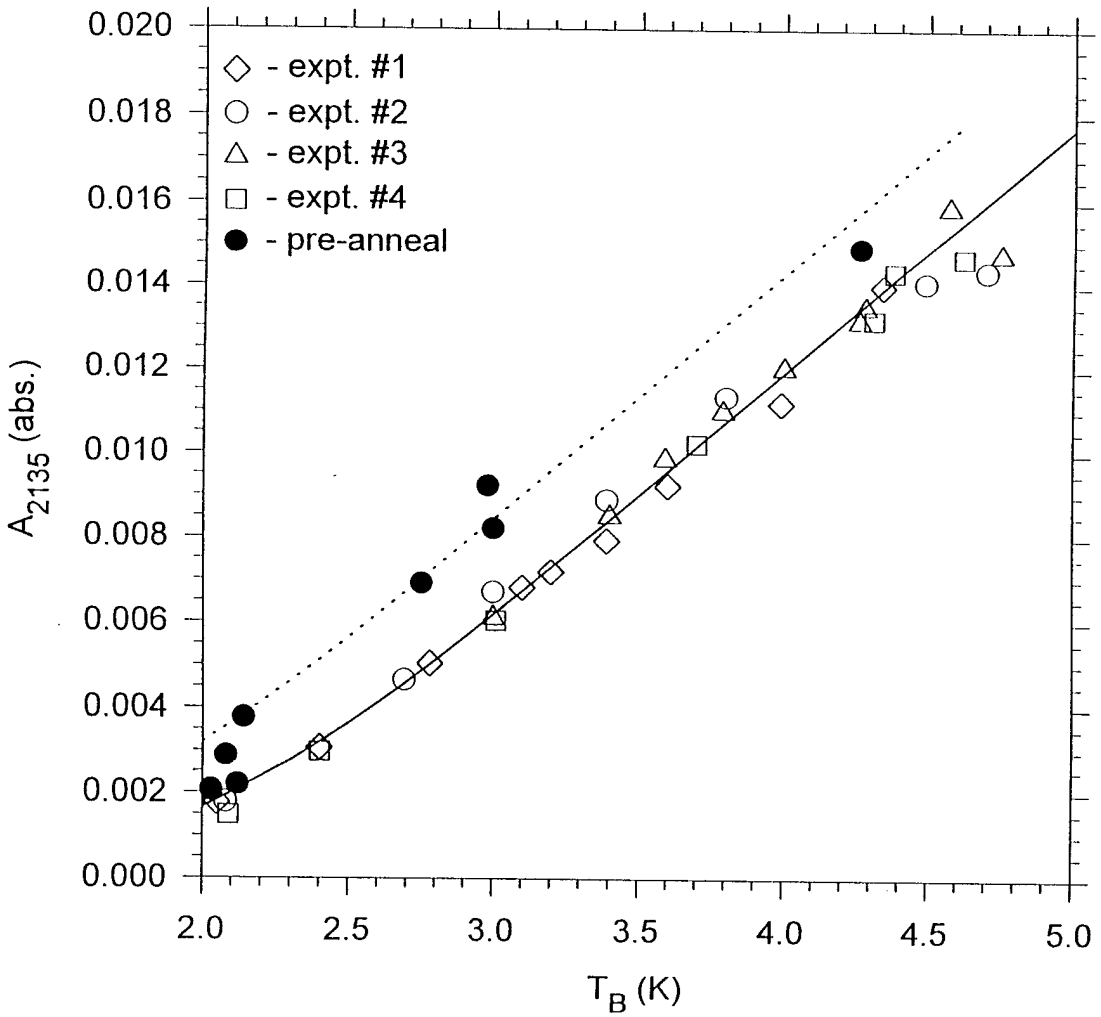
control experiment

CO_2/pH_2 Thermometer Peak





Calibration of CO/pH_2 Thermometer



simplified Boltzmann:

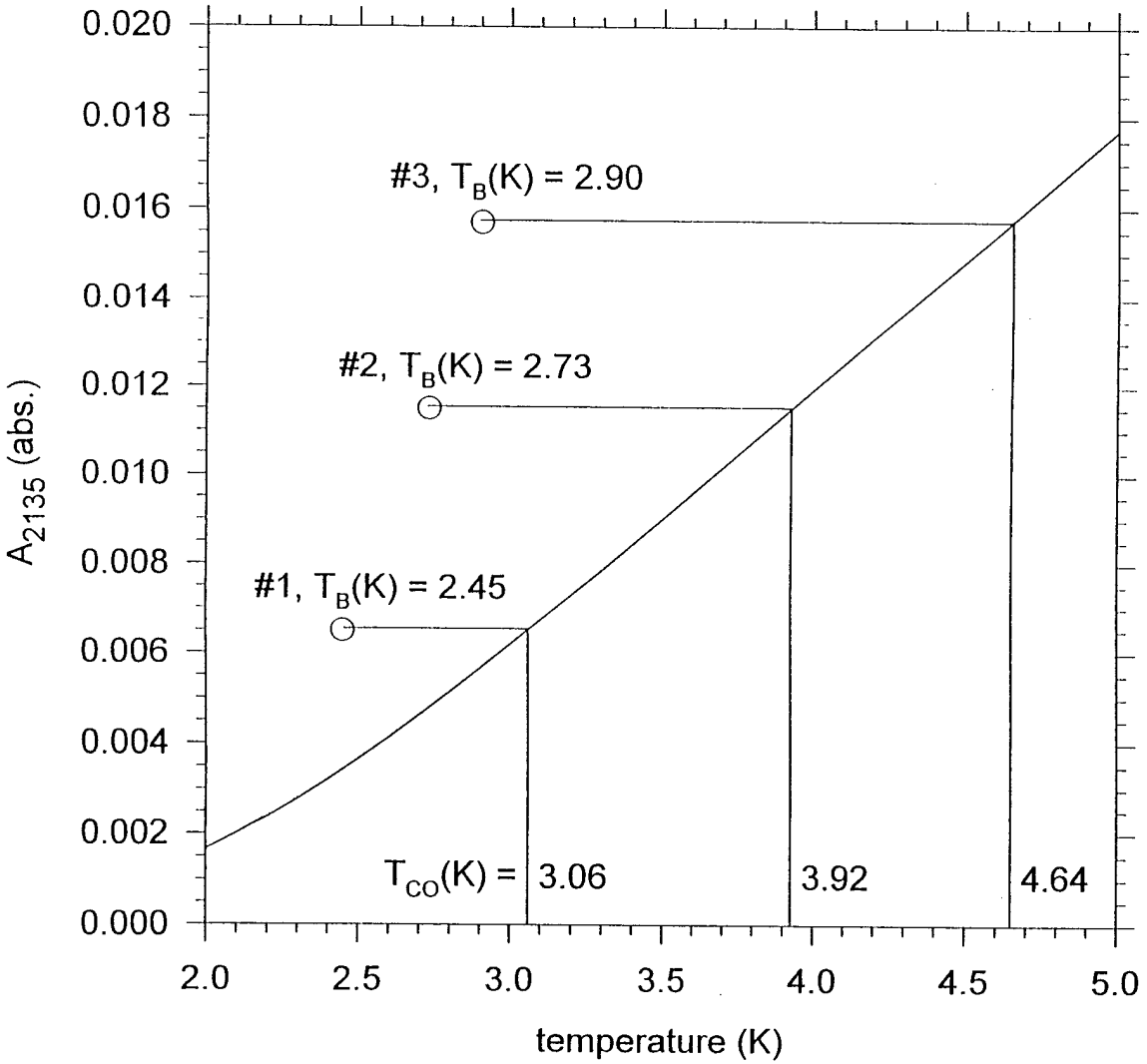
$$A_{2135} = N \exp(-E/T_{CO})$$

$N = 0.0860$
$E = 7.896$ K

include $Q_{rot} \Rightarrow E \approx 11$ K

$6\ B_{CO/pH2} \approx 12$ K

Deposition Temperatures



#3:

Φ_{H2} = 240 mmol/hr

$\dot{R}$ = 55 μm/min

#2:

Φ_{H2} = 200 mmol/hr

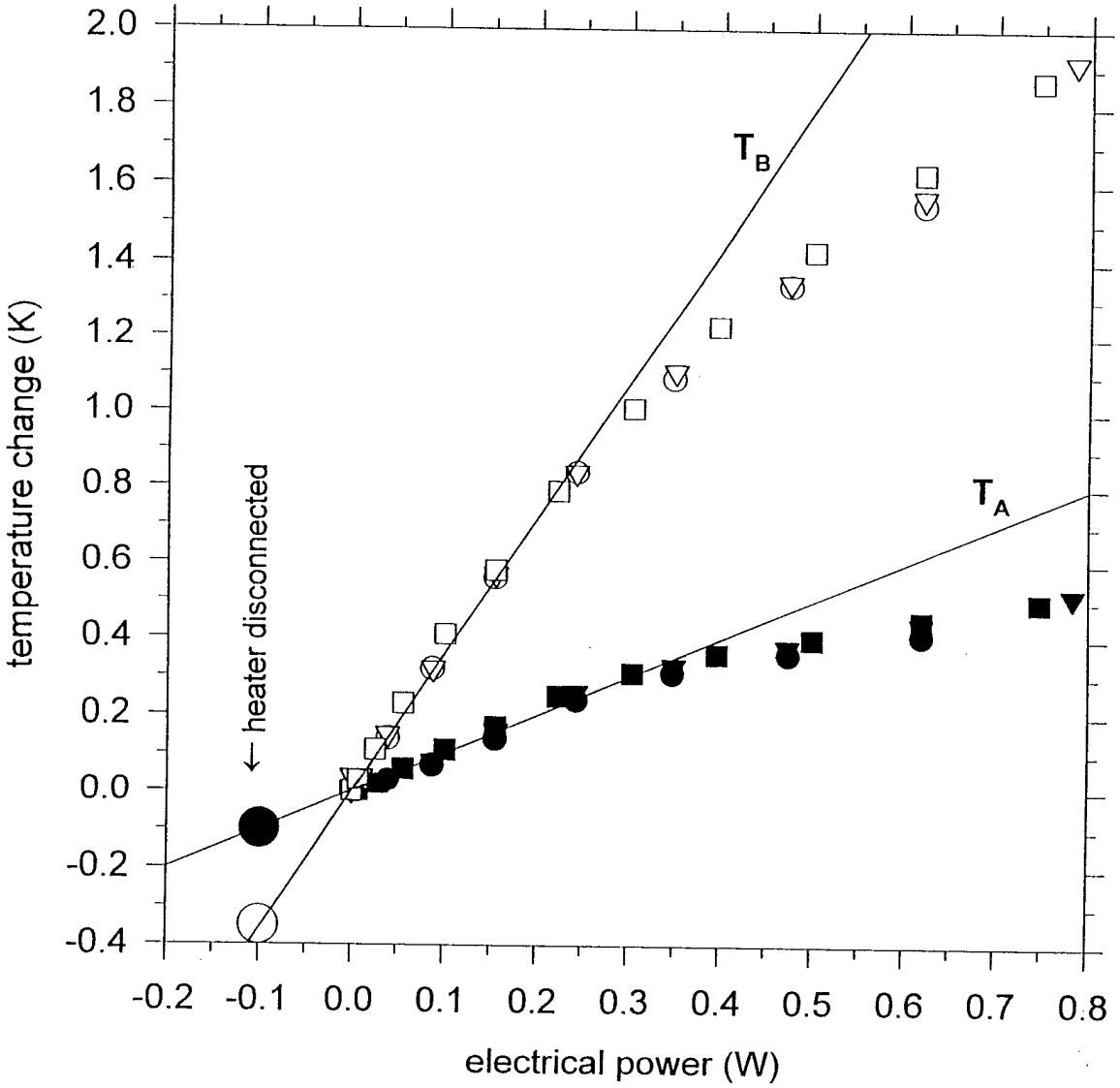
$\dot{R}$ = 48 μm/min

#1:

Φ_{H2} = 110 mmol/hr

$\dot{R}$ = 26 μm/min

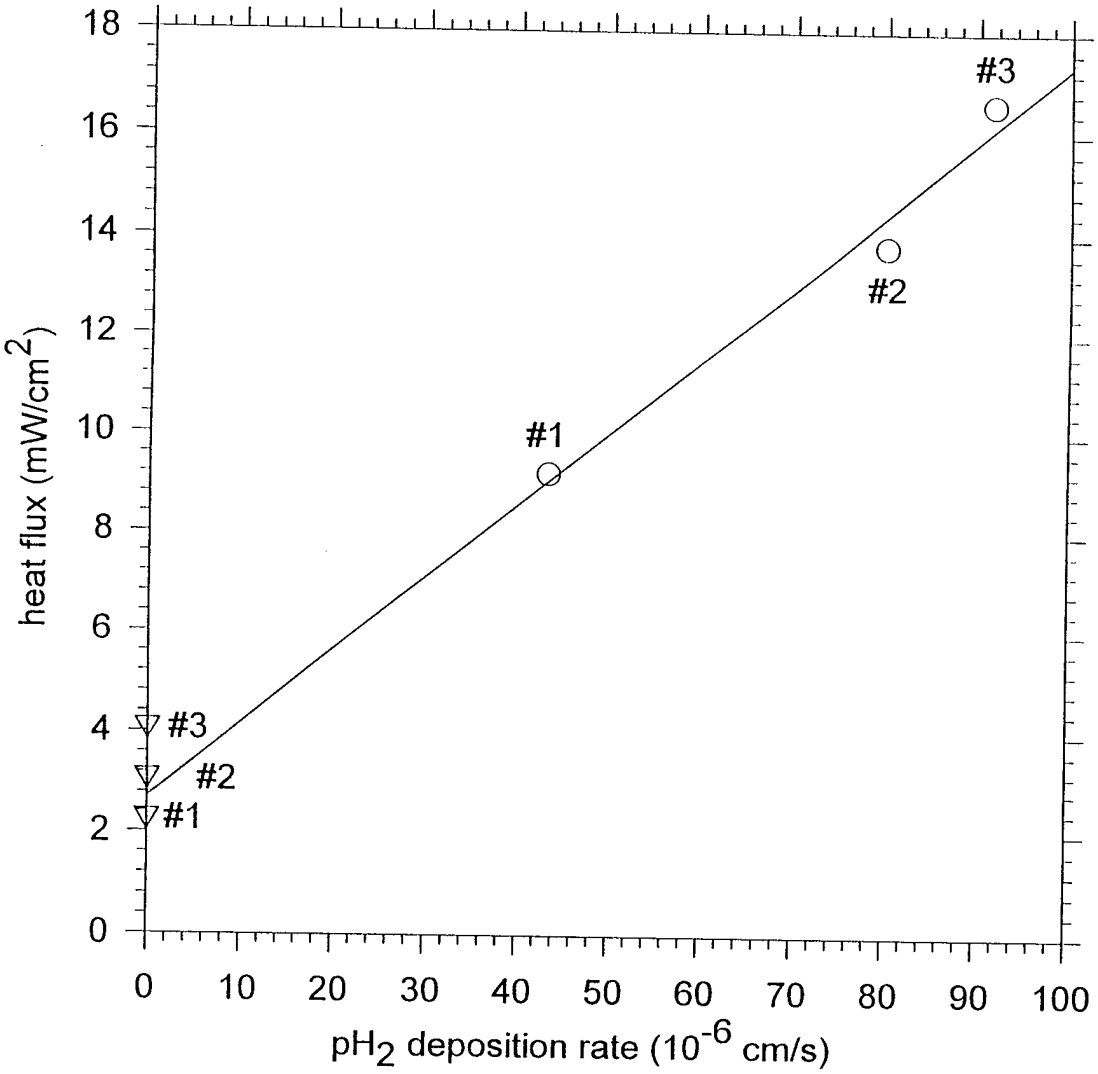
Cryostat Thermal Response



T_B: slope = 3.6 K/W

T_A: slope = 1.0 K/W

Deposition Heat Loads



heat fluxes calculated from
$\Delta T = T_B - T_B(\text{prior dep.})$

slope of fit line $\Rightarrow$
$E_{dep} = 3.3$ kJ/mol

compare with:
$E_{vap} = 1.1$ kJ/mol

← note post-deposition radiative(?) heat loads

3rd International Conference on Cryocrystals and Quantum Crystals, 28 Jul - 4 Aug 2000, Szklarska Poreba, Poland

pH_2 Thermal Conductivity Calculations

expt.#	Δx(cm)	ΔT_{max}(K)	ΔT_{min}(K)	$(\dot{Q}/A)_{max}$	$(\dot{Q}/A)_{min}$	κ_{min}	κ_{max}
1	0.108	0.61	0.21	9.2	6.9	1.2	4.7
2	0.203	1.19	0.79	13.8	10.7	1.8	3.5
3	0.232	1.74	1.34	16.6	12.5	1.7	2.9

Units: $\dot{Q}/A$ (mW/cm^2), κ (mW/cm-K).

Summary: κ = **3(±2) mW/cm-K**, averaged over 2 < T < 5 K range.

Comparison with Literature

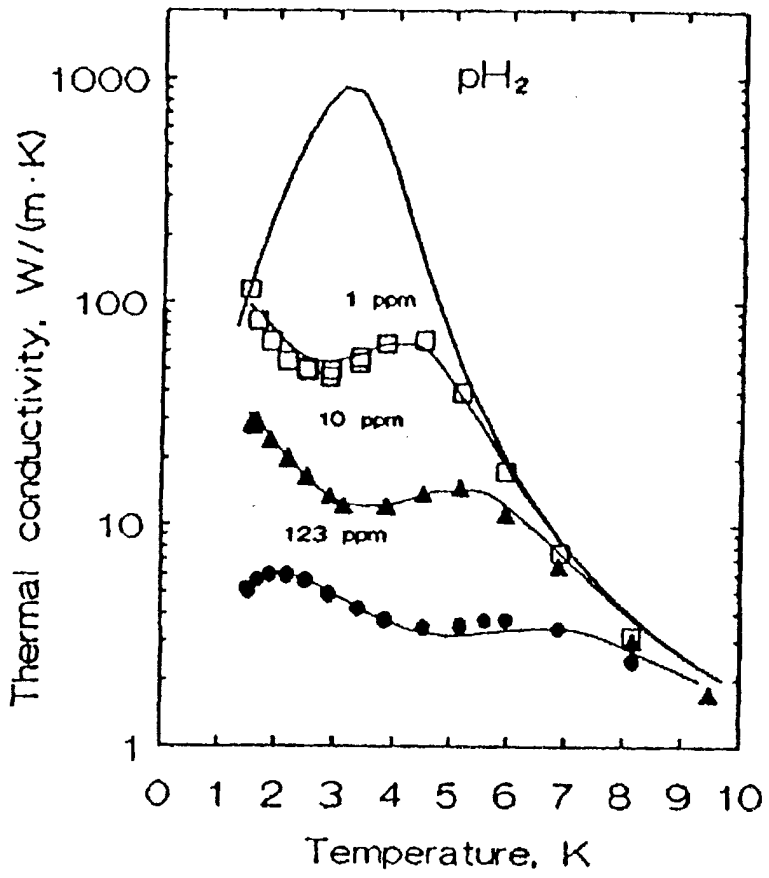


FIG. 1. Thermal conductivity of crystals of pure pH_2 and pH_2 with Ne impurity (the concentration in ppm are indicated); the solid lines are calculated results.

Previous studies on pH_2 solids grown from the gas phase in an enclosed cell near 10 K

$\Rightarrow \quad \bar{\kappa} \approx 4000$ mW/cm-K

& $\quad L_{ph} \sim 0.1$ cm.

$$\kappa = C\, v\, L_{ph} / 3$$

[V.G. Manzhelii, B.Ya. Gorodilov, and A.I. Krivchikov, Low Temp. Phys. **22**, 131 (1996)]

Suggests $L_{ph} \sim 1$ μm in our rapid vapor deposited solids.

Summary

* Demonstrated production of millimeters-thick transparent pH_2 solids by rapid vapor deposition.

* Demonstrated that vapor deposited pH_2 solids are densest close-packed solids, NOT amorphous.

* Demonstrated suitability of vapor deposited pH_2 solids as hosts for high resolution IR absorption spectroscopy of chemically interesting dopants.

* Generalized phenomenon of dopant induced IR activity.

* Exploited CO/pH_2 spectroscopy to probe sample temperature during deposition, and to estimate thermal conductivity.

Collaborators

* Mr. Simon Tam and Ms. Michelle E. DeRose, AFRL/PRSP
  responsible for our experimental data.

* Prof. Takamasa Momose, Kyoto U.
  spectroscopy of CH_4, C_{60}, and CO doped pH_2 solids.

* Prof. Robert J. Hinde, U. Tennessee at Knoxville
  dopant-induced IR absorptions.

* Prof. David T. Anderson, U. Wyoming
  spectroscopy of $(HCl)_2$ in solid pH_2.